

PATENT SPECIFICATION

(11) 1403556

1403556

- (21) Application No. 44323/72 (22) Filed 26 Sept. 1972
 (31) Convention Application No. 2149184 (32) Filed 1 Oct. 1971 in
 (33) Germany (DT)
 (44) Complete Specification published 20 Aug. 1975
 (51) INT CL² C07C 7/10 11/12 11/22
 (52) Index at acceptance
 CSE 7A3 7A5 7AY 9B7B5 9B7B8 9B7BY
 (72) Inventor FRIEDRICH ROTTMAYR



(54) IMPROVEMENTS IN OR RELATING TO THE SEPARATION OF METHYL ACETYLENE AND/OR PROPADIENE FROM ADMIXTURE WITH PROPYLENE AND/OR PROPANE

(71) We, LINDE AKTIENGESELLSCHAFT, a German Company of Wiesbaden, Hildastr. 2-10, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of separating methylacetylene and/or propadiene from admixture with propylene and/or propane.

The gas mixtures produced during the cracking of hydrocarbons in order to produce olefines, consist, depending upon the starting material and the cracking technique used, of varying amounts of inert gases (hydrogen, carbon monoxide, carbon dioxide), lower paraffins, olefines and acetylene, as well as of C_3 and higher, primarily unsaturated, hydrocarbons. In addition, the cracking gases also contain small quantities of methylacetylene and propadiene. The cracking gases are normally compressed, after the heavy oil and cracked gasoline fractions have been separated off, and cooled in stages in counter-flow with cold fractionation products, during the course of which operation, hydrocarbon condensates separate out, and these are fractionated by rectification to produce hydrocarbon fractions each having the same C-number. The crude C_3 fraction thus obtained contains between 75 and 95% of propylene depending upon the cracking conditions: its methylacetylene and propadiene content, the mixture of which will be referred to hereinafter as " C_3H_4 ", ranges between some few tenths of a percent and some few percent; the remainder is propane. The ratio of methylacetylene to propadiene is likewise dependent upon the cracking procedure. The higher the cracking temperature, then the higher the propadiene proportion is likely to be; the methylacetylene-propadiene ratio in a

cracking gas produced under strict conditions, will generally be about 1:1.

Hitherto, the C_3H_4 has been removed from the crude C_3 -fraction by catalytic hydrogenation and the propane by rectification, thus producing polymerisable propylene. Because CO-free hydrogen is required for hydrogenation and the excess hydrogen has to be separated from the hydrogenation product afterwards, this is a somewhat laborious process. Also, of course, it is unsuitable where the C_3H_4 is required as a product.

The extraction of high-purity propylene from the crude C_3 -fraction by rectification alone is a difficult matter, because the boiling points of methylacetylene and propadiene are close to that of propylene, and also probably because a number of binary mixtures of C_3 -hydrocarbons form azeotropes. For the same reasons, the C_3H_4 cannot be obtained by rectification.

It is also known (see German Patent Specification No. 1,468,380), to produce a C_3H_4 -rich cracked gas by the controlled pyrolysis of propylene, to scrub this using an absorption oil after cooling, compressing and removing the CO_2 , and to drive off the C_3 and higher hydrocarbons which go into solution when this happens, by reheating. No method is, however, proposed in this Specification for the separation of the C_3 -fraction obtained in this fashion. The problem of the large-scale separation of the C_3H_4 -hydrocarbons has not therefore been resolved hitherto.

Finally, it is known from German Patent Specification No. 953,700 to use a scrubbing technique in order to remove the acetylene from the gaseous acetylene-ethylene-ethane mixture produced in the fractionation of olefine-rich cracking gas at or just above the liquefaction temperature of the mixture.

It is an object of the present invention to provide a method for the fractionation of a C_3 -fraction consisting of propylene and/or

[Price 33p]

BEST AVAILABLE COPY

propane together with small quantities of methylacetylene and/or propadiene which method is favourable from the energy point of view and makes it possible to extract C_3H_4 in enriched or pure form, and also makes it possible to extract a propylene-propane mixture which is substantially free from methylacetylene and propadiene.

In accordance with the invention, there is provided a method of separating methylacetylene and/or propadiene from admixture with propylene and/or propane in a C_3 -fraction, comprising the step of selectively absorbing the methylacetylene and/or propadiene from the mixture using a polar organic solvent, the absorption being carried out at a temperature such that the selectivity of the solvent for the methylacetylene and/or propadiene (i.e. the ratio of the solubility of propadiene or methylacetylene in the solvent to the solubility of propylene or propane in the solvent) is at a maximum for the absorption pressure used, or does not differ from said maximum by more than 5%.

The theory underlying the invention will now be further discussed with reference to Figures 1 to 3 of the drawings, in which:—

Figure 1 is a graph showing the temperature characteristic of solubility for various C_3 -hydrocarbons in polar solvents;

Figure 2 is a graph of the variation of the ratio of the solubility of propadiene to that of propylene with temperature, using dimethylformamide as solvent at various pressures; and

Figure 3 is a graph of the variation of the selectivity maximum for the system of Figure 2, with pressure.

The method in accordance with the invention makes it possible to separate the C_3H_4 hydrocarbon from mixtures which include propylene and/or propane under optimum conditions. The behaviour of the solubilities of the individual C_3 -hydrocarbons in relation to one another can be seen from Figure 1 where the temperature characteristics of the solubility λ of methylacetylene (curve A), propadiene (curve B), propylene (curve C), and propane (curve D), in conventional, polar, organic acetylene solvents, in each case at 1 atm. absolute, have been plotted. It can be seen from this graph that the solubility of propane is lower than that of propylene and that the solubility of propadiene is lower than that of methylacetylene. Thus, it is particularly simple to remove C_3H_4 from a mixture containing propane alone. If it is required to absorb both the methylacetylene and the propadiene, then the quantity of scrubbing agent used will be adjusted to the solubility of the propadiene; this thus ensures complete absorption of methylacetylene. If, in the presence of propadiene, it is simply required to remove methylacetylene, then the requisite quantity

of solvent is smaller because of the higher solubility of the methylacetylene; only part of the propadiene is removed in this process. Finally, if the C_3 -mixture contains only methylacetylene or only propadiene in addition to propylene and/or propane, then these (methylacetylene or propadiene) can also be selectively and individually absorbed by the method of the invention.

As already mentioned, the selective absorption of acetylene from a C_2 -mixture, the most favourable scrubbing temperatures are near the dewpoint of the mixture being scrubbed. In the course of investigations upon which the present invention is based and the results of which are illustrated graphically in Figures 2 and 3, however, it was surprisingly discovered that the dewpoint is by no means the most favourable scrubbing temperature where the selective absorption of C_3H_4 from a C_3 -mixture is concerned, and indeed that, at higher pressures, C_3H_4 cannot be removed at all the condensation point. The present invention is based upon the recognition that the selectivity of a polar, organic solvent towards the pair propadiene/propylene, i.e. the ratio of the solubility of propadiene to the solubility of propylene (λ propadiene: λ propylene) first rises with increasing temperature, commencing from the condensation temperature of the gas mixture being scrubbed, passes through a maximum and then falls again. This law, as the family of curves of Figure 2 shows, applies irrespective of the absorption pressure: Curve I indicates the results for the solvent dimethylformamide at an absorption pressure of 1 atm. absolute; curve II at 2 atm. absolute; curve III at 3 atm. absolute; curve IV at 9 atm. absolute; and curve V at 16 atm. absolute. Here, the maximum shifts towards higher temperatures and lower values of maximum selectivity as the pressure increases; at the same time the maximum becomes flatter. The position of the various maxima is indicated substantially by the broken-line curve. The temperatures T_I (-48°C), T_{II} (-32°C), T_{III} (-21°C), T_{IV} (15°C) and T_V (36°C), plotted upon the abscissa are the condensation temperatures of the mixture being scrubbed at the corresponding pressure of 1, 2, 3, 9 and 16 atm. absolute.

For the family of curves shown in Figure 2, it is possible to determine the particular optimum scrubbing temperature for the desired absorption pressure. It is 30 to 40°C above the dewpoint of the mixture at the selected pressure. Even at a selectivity which deviates by about 5% from the peak selectivity, the scrubbing process can still be carried out with advantage, because of the relatively flat profile of the curves in the neighbourhood of the maxima; this deviation corresponds to a temperature deviation of ± 10 to 15°C from the selectivity maximum.

Finally, Figure 2 also shows that the selectivity is one or less under certain conditions of temperature and pressure. From the definition of selectivity as λ -propadiene; λ -propylene, it follows that selectivity absorption of propadiene is not then possible.

The selectivity maximum is distinguished by the fact that at this point the internal throughput in the scrubbing system, and therefore that proportion of the total energy required assignable to this throughput, is at its lowest. The quantity of scrubbing agent can of course be further reduced if the absorption temperature is selected to be below that corresponding to the selectivity maximum, because then the solubility of the propadiene increases. However, the investigations carried out for the purposes of the invention have shown that the internal throughput then increases so radically that the total energy requirement rises, despite the reduced quantity of solvent used. The minimum energy requirement is therefore practically coincidental with the peak selectivity.

In Figure 3, the dependence of the selectivity maximum upon the pressure for the pair, propadiene and propylene, using as solvent dimethyl formamide, has been plotted. It is evident that the maximum selectivity first of all slowly falls as the pressure increases and as the pressure gradually rises further, drops very rapidly. The absorption pressure is therefore conveniently selected to be lower than the pressure at which the steep drop in maximum selectivity commences. Taking as an example, the pair propadiene/propylene and the solvent dimethyl formamide, the steep drop commences at about 2.0 atm. absolute, that is to say at a selectivity maximum of about 4.2. It is best to carry out the absorption of propadiene in dimethyl formamide at a scrubbing pressure of 1 atm. absolute, corresponding to a selectivity maximum of about 5. If the C_3 -fraction is available under high pressure, then it is preferably expanded prior to absorption, to a pressure which is within the range given above, and then recompressed after absorption. The energy loss due to expansion, is more than compensated for by the reduced energy requirement for the absorption at the lower pressure, especially if the cold produced at the time of expansion is made use of.

The numerical values contained in Figures 2 and 3 relate, as already mentioned, to the selectivity of dimethyl formamide for the pair propadiene/propylene; the values for the solvent N-methyl pyrrolidone differ only very little from this. Other polar, organic solvents can quite generally be used to carry out the method of the invention. In the case of the polar, aprotic solvents, which boil at temperatures higher than 100°C, these including not only dimethyl formamide and N-methyl pyrrolidone, but also dimethyl acetamide,

diethyl formamide, butyrolactone, tetramethylurea, dimethyl sulfoxide, acetylacetone and hexamethyl phosphoric acid triamide, the selectivity maxima are particularly well defined. Basically, the same applies equally where it is the solubility of methyl acetylene which is the governing factor and where, to, it is not propylene but propane which represents the component having the poorer solubility.

The method in accordance with the invention opens up several possibilities of using the C_3 -fractions; if the apparatus and the quantity of scrubbing agent are appropriately designed, then the head product of the absorption will take the form of a virtually C_3H_4 -free propylene-propane mixture (<10 ppm methylacetylene + propadiene) from which, advantageously, by a subsequent propylene-propane rectification operation, pure polymerisable propylene can be produced.

Irrespective of what the final C_3H_4 content in the head product of the absorption column is to be, and irrespective therefore of whether or not polymerisable propylene is to be produced, the method of the invention makes it possible for the first time to separate C_3H_4 , either in the pure form, or in the form of a C_3 -mixture heavily enriched with C_3H_4 , depending upon how the charged solution is regenerated. Pure C_3H_4 , because of its extraordinarily high reactivity, is a valuable starting material for use in synthesis and for the manufacture of polymers. In admixture with propylene and propane and other hydrocarbons, C_3H_4 can also be used as a substitute for acetylene in welding and cutting operations. If the separation of the C_3H_4 is to be used primarily for the production of methylacetylene, then it is a good idea to adapt the amount of solvent used to the solubility of the methylacetylene, only part of the propadiene being removed during the scrubbing operation. Because the quantity of solvent required for this purpose is only approximately half that required for the absorption of propadiene, this method can be carried out at a very low cost.

A C_3 -mixture containing at least 50% by volume of C_3H_4 can be extracted from a C_3 -fraction which is at high pressure, in accordance with a preferred embodiment of the invention, by carrying out the absorption at the high pressure; expanding the charged solution and first of all freeing it by stripping from part of the co-dissolved propylene and propane, and then freeing it from the remaining propylene and/or propane, as well as the C_3H_4 , by subsequent regeneration at a pressure which is again reduced, the C_3H_4 concentration of the stripping gas being so chosen that from the solution which is in equilibrium with it during stripping, a C_3 -mixture of the desired C_3H_4 -concentration is driven off in the subsequent regeneration

column. The stripping gas of the requisite composition can advantageously be obtained by supplying part of the gas mixture driven off from the solution in the regenerating column to part of that gas mixture, having a low C_2H_2 -content, which is liberated by expansion of the charged solution coming from the absorption column to a pressure intermediate between the pressure of the absorption column and that of the stripping column.

In order to extract pure C_2H_2 , by way of stripping gas pure C_2H_2 obtained as the head product from the regeneration column may be used.

In accordance with a further feature of the invention, the solvent is heated after contact with the gas being scrubbed in the reboiler section of the absorption column, so that part of the co-dissolved propylene/propane is already degassed here. In choosing the reboiler temperature, it should be ensured that the stability of the solvent and of the C_2H_2 is not jeopardised. Within the temperature range extending the upper temperature limit thus determined, the reboiler temperature is matched to the desired C_2H_2 -concentrations; it will be made the higher, the lower the proportion of co-dissolved propylene and propane which can be allowed in the solution leaving the reboiler section.

The extraction of C_2H_2 , finally, can also be improved by arranging that, prior to absorption, part of the propylene is removed by rectification. In this way, the quantity of gas to be scrubbed, and therefore the energy consumption for the absorption phase, are reduced to such an extent that the energy requirement for the overall process is less than when carrying out C_2H_2 -extraction by absorption alone. In addition, there is the fact that pure propylene is made available as a valuable by-product. The difficulties previously referred to in rectifying a C_2H_2 -containing C_2 -fraction do not arise here because only a part, e.g. half, of the propylene is to be removed by rectification.

In accordance with another feature of the invention C_2H_2 may be obtained from a C_2 -fraction at a super atmospheric pressure, of more than 2 atmos absolute by expanding this fraction to a pressure of less than 2 atm. absolute, preferably 1 atm. absolute, the cold being recovered at the same time, and subjecting the expanded fraction at this pressure to selective absorption to remove the C_2H_2 , the temperature in the reboiler section of the absorption column being so chosen that the concentration ratio of C_2H_2 to propylene and propane, corresponds with the desired concentration ratio in the end product obtained by regeneration of the solution leaving the reboiler section.

Apparatus for carrying out the method of the invention may comprise an absorption

column designed for high-pressure operation, with a feed line for the gas which is to be scrubbed, an absorber section, condenser section and reboiler section, and with an extraction line leading from the column head to carry off the scrubbed gas, a stripping column designed for lower pressure operation and connected to the sump of the absorption column through an expansion valve, a regeneration column designed for operation as approximately atmospheric pressure, its head being connected with the sump of the stripping column both via a line carrying the charged solution and provided with an expansion valve, and via a stripping gas line equipped with a compressor and branching from the line carrying the C_2H_2 -product, and finally lines for regenerated solvent leading from the sump of the regeneration column in each case through a solvent pump, respectively to the head of the absorption column and the head of the stripping column.

The apparatus also advantageously includes a separator designed for use at a pressure slightly above the stripping column pressure, which separator is arranged in the line leading from the sump of the absorption column to the stripping column, from the gas and liquid space of the separator in each case a line containing an expansion valve leads to the stripping column, the gas space of the separator also communicating through a valved line with the stripping gas line leading from the head of the regeneration column.

The invention will now be further described with reference to Figures 4 and 5 of the drawings, which are flow-sheets for two respective embodiments of the invention.

Referring to Figure 4, 10,360 Nm³ of a C₆-fraction which has been produced in a bracking gas fractionation plant (not shown), and is at a pressure of 16 atm. absolute and at the dewpoint temperature (36°C), is fed to the C_2H_2 -separation process through a line 1. The C_2 -fraction contains 180 Nm³ each of methylacetylene and propadiene, as well as 270 Nm³ of propane; the remainder consists of propylene, together with a small quantity of C₄-hydrocarbons. This C_2 -mixture is fed in gaseous form to the scrubbing section α of a reboiler-absorber column 2; the temperature in the scrubbing section α is maintained at about 70°C, i.e. the temperature at which, in accordance with Figure 2, the selectivity maximum is located at a scrubbing pressure of 16 atm. absolute (see curve V). Through a line 3, about 105 t of dimethyl formamide (DMF) at a temperature of between 35 and 45°C are fed to the scrubbing section. The solvent becomes saturated on the upper bubble cap trays of the column 2 with propylene and propane, and because of the heat of solution, acquires a temperature of about 70°C. The scrubbed gas is finally restored to its initial temperature of 36°C

in section *b* of the reboiler-absorber 2 by means of a cooler 4. In so doing, a small quantity of propylene and propane condenses out and this is virtually completely washed out by the DMF vapours rising from the upflowing gas. At the head of the column 2, through a line 5 a gas mixture is drawn off which consists of 4300 Nm³ of propylene and propane with a residual content of about 0.3% by volume of C₃H₄.

The solvent drips down through the plates of the scrubbing section *a* and finally over those of the reboiler section *c*, and is heated up at the bottom to about 150°C by steam. In so doing about 8300 Nm³ of propylene and propane co-dissolved in the section *a*, are liberated, flowing upwards and being re-absorbed in the section *a*. The sump liquid, in which in addition to C₃H₄ there is still about 5700 Nm³ of propylene and propane dissolved, is expanded to 4 atm. absolute through a valve 6, about 4400 Nm³ of propylene and propane thus being connected to the gas phase. The gas liquid mixture is fed into a separator 7 where the gas is separated from the liquid. Of the gaseous fraction, which contains no C₃H₄, about 134 Nm³ are branched off through a valve 8 and, as described hereinafter, employed as stripping gas. The remainder of the liberated gas mixture, about 4266 Nm³, is introduced through a valve 9 and a line 10 into a stripper-absorber column 11, which operates at 3 atm. absolute. The liquid from the separator 7 containing the C₃H₄ and about 1300 Nm³ of propylene, likewise passes into the column 11 through a valve 12 and a line 13.

In this example, a C₃-mixture consisting of 50% propylene and propane, and 50% C₃H₄ is to be produced by way of product. The stripper-absorber 11 must therefore be operated so that from its sump a solution can be drawn off which contains equal mole quantities of C₃H₄ and propylene/propane in solution. The gas phase, which is in equilibrium with such a solution at the sump temperature of 150°C and the column pressure of 3 atm. absolute, has the following composition as far as the hydrocarbon proportion is concerned: 41 Mol% C₃H₄ and 59 Mol% propylene/propane; this means that the stripping gas must have the indicated composition. It is produced by the introduction into the stripper-absorber 11 of 612 Nm³ of the product obtained in the ensuing regeneration column and consisting of 50% C₃H₄ and 50% propylene and propane, through a line 14 and a compressor 15, together with 134 Nm³ of the propane-containing propylene, free from C₃H₄, branched off through the valve 8 into a line 16 and coming from the separator 7, this through line 17.

The gas mixture rising through the

stripper-absorber 11, is scrubbed using 70 t of DMF which is supplied through a line 18 at a temperature of 10°C. From the head of the column, there escapes through a line 19 a mixture of 5,376 Nm³ of propane-containing propylene and about 18 Nm³ of C₃H₄, at a temperature of around 30°C. In a compressor 20, this is raised to the pressure of the gas mixture leaving the head of the column 2, and mixed therewith, the mixture leaving the plant through a line 21. Thus, a total of 9712 Nm³ of a propane-containing propylene are produced, contaminated with 36 Nm³ of C₃H₄. Because propadiene is less readily soluble than methylacetylene, the contaminant consists virtually exclusively of propadiene.

The liquid in the sump of the column 11 contains 630 Nm³ each of C₃H₄ and propylene/propane. It is drawn off through a line 22, expanded through a valve 23 to the pressure of a regeneration column 24, namely 1.5 atm. absolute, fed to the head of the column 24 and there freed from the dissolved C₃-hydrocarbons, in counterflow with a rising gas-vapour mixture. From the gas leaving the head of the column 24, the solvent vapours are first condensed out in a water cooler 25 and recycled to the column 24. Through a line 26, 1260 Nm³ of a mixture comprising 50% methylacetylene plus propadiene, and 50% propane-containing propylene are withdrawn from the cooler 25, of which 648 Nm³ are available for withdrawal through a line 27 as product, whilst 612 Nm³, as previously described, are branched off to serve as stripping gas through the line 14.

The regenerated solvent is passed through a water-cooler 28 and is then in part fed by a pump 29 through a further heat-exchanger 30 cooled by evaporating propylene, to the stripper-absorber column 11, and in part by a pump 31 through the line 3 to the absorption column 2.

The quantity of propane-containing propylene to be injected through the valve 8 and the line 16 into the stripping gas line 17, is the smaller the larger the desired C₃H₄-concentration in the end product withdrawn through the line 27. In practical operation, the desired concentration will be adjusted by corresponding control of the valve 8. If pure C₃H₄ is to be obtained at 27, then the valve 8 remains closed; then from the head of the regenerating column 24, pure C₃H₄ is recycled to the stripper-absorber 11.

By means of the method described, it is possible to obtain as head product from the regeneration column 24, pure C₃H₄, or a C₃-mixture heavily enriched with C₃H₄, and as head product from the reboiler-absorber or stripper-absorber, a propane-containing propylene contaminated with C₃H₄. The same method can also, in principle, be used

to produce, on the one hand pure or enriched C_3H_4 and, on the other hand propane-containing propylene which contains no C_3H_4 ; it is merely necessary by increasing the quantity of the scrubbing agent used and designing the columns appropriately, to ensure that the C_3H_4 is completely washed out of the rising C_3 -mixture. The internal throughputs, and with them the energy requirement, rise fairly steeply in so doing. In this way, a propane-containing propylene with less than 10 ppm of propadiene and less than 5 ppm DMF, can be withdrawn at 21, which, if required, can be fractionated by rectification thereafter without any difficulty to produce polymerisable propylene, and propane.

In a variation of the method described, a preliminary rectification is used to remove part of the propylene from the C_3 -mixture which is to be treated, prior to the absorption step, thus reducing the quantity of gas which is subjected to absorption. The C_3 -fraction, supplied to the installation in a quantity of 10,360 Nm³ at 16 atm. absolute and 36°C and 360 Nm³ of C_3H_4 and 270 Nm³ of propane, is fractionated by rectification, to give 5000 Nm³ of pure, polymerisable propylene and 5360 Nm³ of a C_3 -mixture which contains all the C_3H_4 and all the propane. Then, from this C_3 mixture, by the method illustrated in Figure 4, either pure or heavily enriched C_3H_4 and also either C_3H_4 -free or C_3H_4 -contaminated propane-containing propylene are obtained.

Another possible method of further processing the C_3 -mixture obtained by rectification of the crude C_3 -fraction, will now be described with reference to Figure 5.

From a C_3 -fraction (10,360 Nm³, of which 360 Nm³ is C_3H_4 and 270 Nm³ is propane, the remainder being propylene; temperature 36°C; pressure 16 atm. absolute) coming from a cracking gas fractionation stage, as previously described, 5000 Nm³ of polymerisable propylene and 5360 Nm³ of a C_3 -mixture (of which 360 Nm³ is C_3H_4 and 270 Nm³ is propane, the remainder being propylene) are obtained by a preliminary rectification. The C_3 -mixture is then expanded to 1 atm. absolute through a valve 40, the cold liberated in the expansion being transferred in a heat-exchanger 41 to another medium passing through the gas fractionation system. At a pressure of 1 atm. absolute, the selectivity maximum, as Figure 2 shows, is at -10°C (curve I). The heat-exchanger 41 is therefore so designed that the C_3 -mixture leaves it at -10°C. The mixture is then injected through a line 42 into a scrubbing column 43 and there scrubbed using 123 t of DMF cooled to about -5°C, this being fed through a line 44 to the column. Above the solvent input, the scrubbed gas is sprayed with liquid propylene and

propane which is produced by condensation in a cooler 45. The gas is cooled to the dewpoint i.e. about -48°C. The propylene-propane condensate serves to make good the heat of solution which is liberated with saturation of the solvent by the individual components of the C_3 -mixture, and at the same time to practically completely remove the DMF vapours from the scrubbed gas. From the head of the column 43 through a line 46, 4746 Nm³ of propane-containing propylene, with a content of less than 10 ppm of C_3H_4 and less than 5 ppm of DMF, are drawn off. The cold gas is heated in a heat-exchanger 47 in counterflow with a medium (from the gas fractionation system) which is to be cooled, and then compressed by a compressor 48 back to the original pressure of 16 atm. absolute.

The sump liquid of the scrubbing column 43, at a temperature of about -10°C, is fed to a reboiler 49 and there heated to about 100°C. The gas liberated in the process is recycled through lines 50 and 42 to the scrubbing column 43. The liquid leaving the reboiler 49 still contains 254 Nm³ of propylene and propane, and 360 Nm³ of C_3H_4 . This solution is fed by a pump 51 to a heat-exchanger 52 where it is further heated and thence to a regeneration column 53 where it is degassed at around 150°C. At the head of the column 53, about 614 Nm³ of the mixture of about 58% of C_3H_4 and 42% propylene and propane, escapes. In a water-cooler 54 and a cooler 55, which is operated with evaporating propylene, the entrained solvent vapours are condensed out of the escaping mixture and recycled through a line 56 to the column 53. The C_3H_4 -product is withdrawn through a line 57 at a temperature of -15°C.

The regenerated solvent is cooled in the heat-exchanger 52 and a further heat-exchanger 58 to about 110°C and is then used to heat the reboiler 49, its temperature dropping further to about -5°C. Through the line 44, the solvent is then recycled to the column 43.

The C_3H_4 -concentration in the solvent leaving the reboiler, and therefore the C_3H_4 -content of the end product drawn off through the line 57, can be regulated by adjusting the temperature at the bottom of the reboiler 49. If the end product is to be more heavily enriched in C_3H_4 , then a still higher reboiler temperature will be required.

The expansion of the gas and the separating of the methylacetylene and propadiene at 1 atm. absolute, and the ensuing recompression of the scrubbed gas, required less energy than scrubbing under pressure. Moreover, the stripper-absorber can be discarded. The regulation of the desired C_3H_4 -concentration by the adjustment of the temperature at the

base of the reboiler is particularly simple from the operational point of view.

WHAT WE CLAIM IS:—

1. A method of separating methylacetylene and/or propadiene from admixture with propylene and/or propane in a C_3 -fraction comprising the step of selectively absorbing the methylacetylene and/or propadiene from the mixture using a polar organic solvent, the absorption being carried out at a temperature such that the selectivity of the solvent for the methylacetylene and/or propadiene (i.e. the ratio of the solubility of propadiene or methylacetylene in the solvent to the solubility of propylene or propane in the solvent) is at a maximum for the absorption pressure used, or does not differ from said maximum by more than 5%.
2. A method as claimed in Claim 1, wherein the absorption pressure used is below the pressure at which the steep drop in the maximum selectivity/absorption pressure curve commences.
3. A method as claimed in Claim 1 or Claim 2, wherein said solvent is a polar, aprotic solvent having a boiling point above 100°C.
4. A method as claimed in Claim 3 as dependent on Claim 1 wherein said solvent is dimethyl formamide or N - methylpyrrolidone, and wherein absorption in the required temperature range is ensured by carrying out the absorption at a temperature which is between 30° and 40°C higher than the condensation temperature of said C_3 -fraction at the absorption pressure used.
5. A method as claimed in Claim 3 or Claim 4 as appendant to Claim 2, wherein said C_3 -fraction is at a pressure above the required absorption pressure; wherein said C_3 -fraction is expanded prior to absorption to a pressure not exceeding 2 atm. absolute, and is subsequently scrubbed with dimethyl formamide; and wherein the propylene and/or propane thus wholly or to a large extent freed from methylacetylene and/or propadiene is recompressed to the original pressure of the initial C_3 -fraction.
6. A method as claimed in Claim 1, or Claim 3 as appendant to Claim 1, or Claim 4 as appendant to Claim 1 or Claim 3, for the production of a mixture containing at least 50% by volume of methylacetylene and/or propadiene from a C_3 -fraction which is at a superatmospheric pressure above 2 atm. absolute, wherein the absorption step is carried out at this superatmospheric pressure;

and wherein the charged solution leaving the absorption step is expanded and first freed by stripping from part of the co-dissolved propylene and propane, and then freed from the remaining propylene and/or propane by a subsequent regeneration after a further reduction in pressure, the concentration of methylacetylene and/or propadiene in the stripping gas being so selected that from the solution which is in equilibrium with the stripping gas at the time of stripping, a C_3 -mixture having the desired concentration of methylacetylene and/or propadiene is driven off in the ensuing regeneration step.

7. A method as claimed in Claim 6, wherein the stripping gas is obtained by mixing part of the gas mixture driven off from the solution in the regeneration step to part of the gas mixture, low in methylacetylene and/or propadiene which is liberated on expansion of charged solution leaving the absorption step and the pressure used in the stripping step.

8. A method as claimed in Claim 6 for the production of substantially pure methylacetylene and/or propadiene, wherein as the stripping gas, there is used methylacetylene and/or propadiene leaving the head of the regeneration column used in the regeneration step.

9. A method as claimed in any one of the preceding Claims, wherein said solvent, after contact with the gas which is to be scrubbed in the reboiler section of an absorption column, is heated until part of the slowly-dissolving propylene and/or propane is degassed therefrom.

10. A method as claimed in any one of the preceding Claims, wherein, prior to the absorption step, part of the propylene present in the initial mixture is removed by rectification.

11. A method as claimed in any one of Claims 1 to 5, or in Claim 9 or Claim 10 as appendant thereto wherein said C_3 -fraction is at a superatmospheric pressure of more than 2 atm. absolute; wherein said C_3 -fraction is expanded to a pressure of not more than 2 atm. absolute, the cold produced being recovered, and the expanded fraction subjected at this pressure to selective absorption of methylacetylene and/or propadiene, the temperature in the reboiler section of the absorption column used being so chosen that the concentration ratio of methylacetylene and/or propadiene to propylene and/or propane corresponds to the required concentration ratio in the end-product

obtained on regeneration of the solution leaving said reboiler section.

- 5 12. A method of separating methylacetylene and/or propadiene from admixture with propylene and/or propane, substantially as hereinbefore described with reference to Figures 1 to 3, or Figure 4, or Figure 5 of the drawings.

For the Applicants,
G. F. REDFERN & COMPANY,
St. Martin's House,
177 Preston Road,
Brighton—Sussex,
and
317 High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

1403556

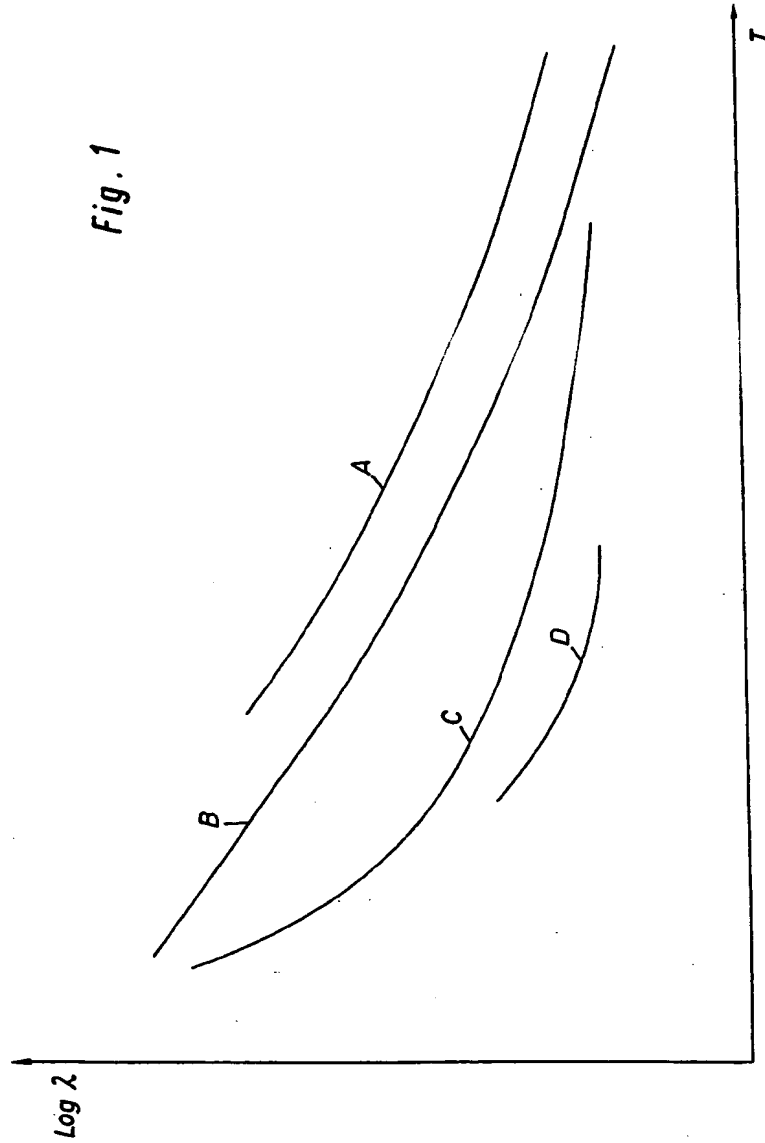
COMPLETE SPECIFICATION

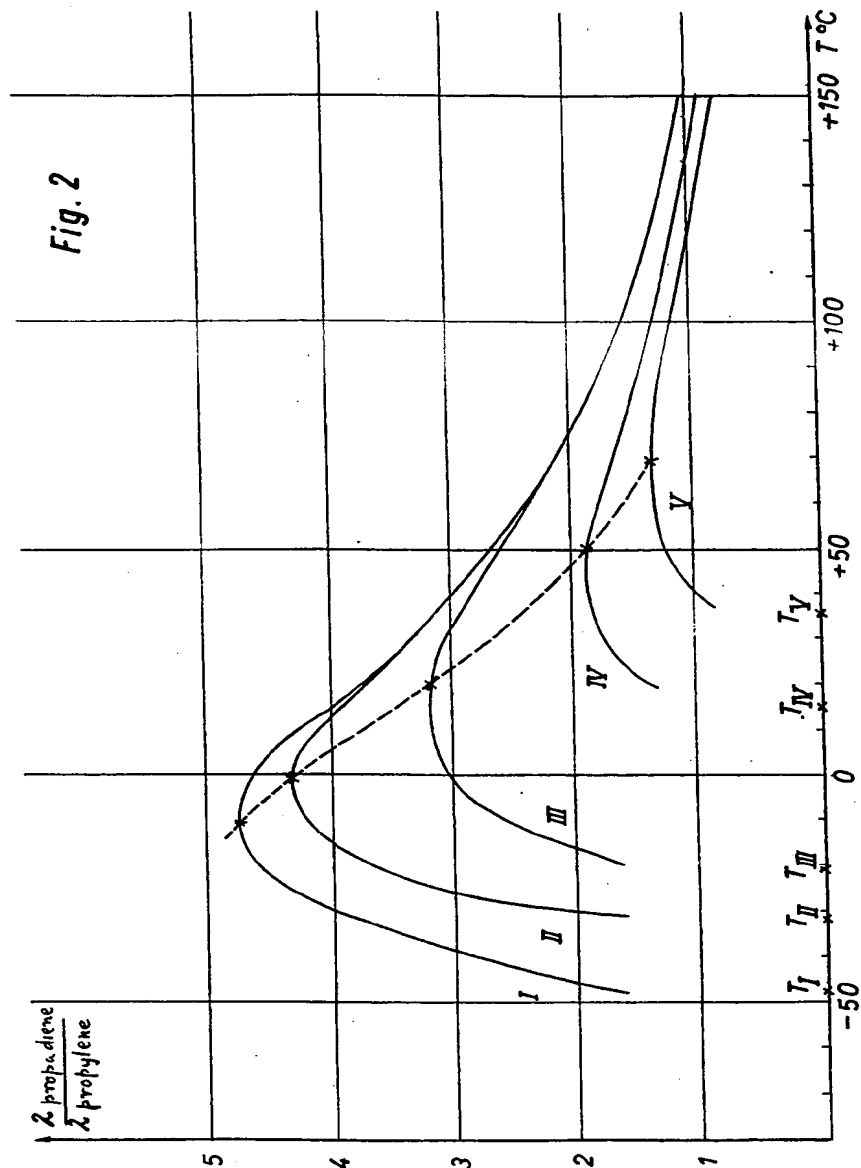
5 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 1

Fig. 1





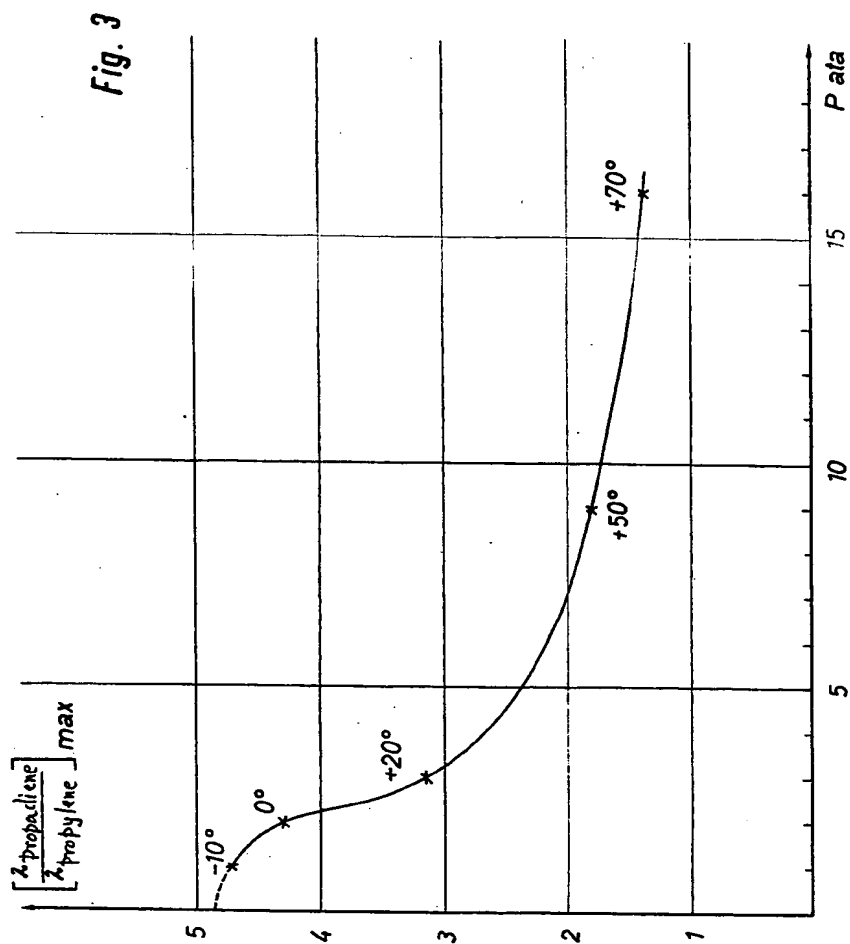
1403556

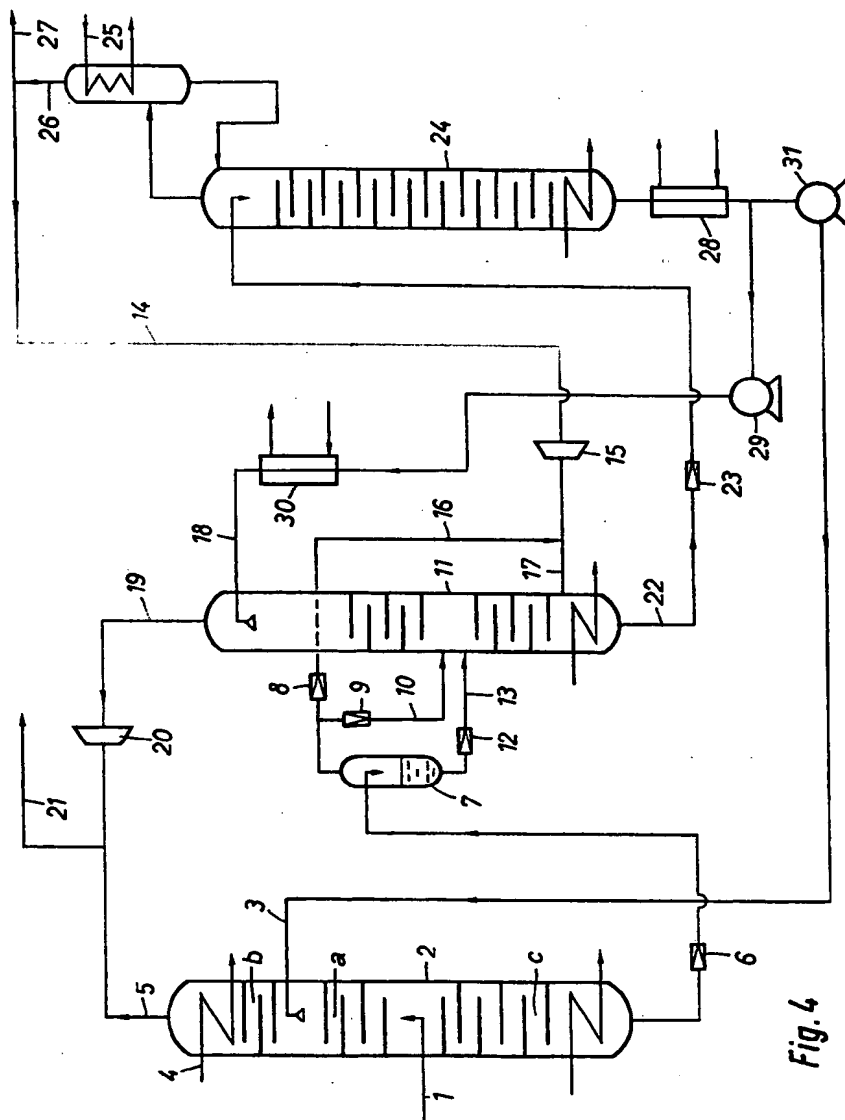
COMPLETE SPECIFICATION

5 SHEETS

This drawing is a reproduction of
the Original on a reduced scale

Sheet 3





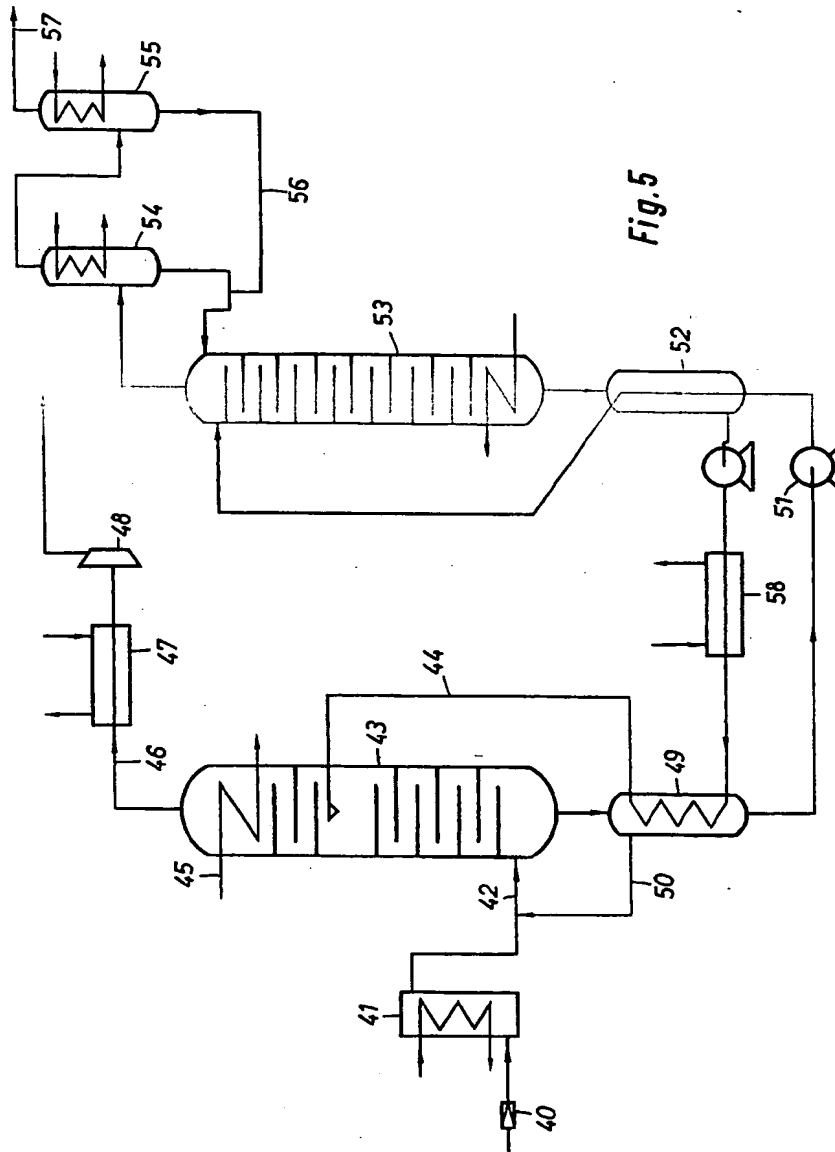


Fig. 5

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.